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DFT modeling of the carbon dioxide and alkene oxide reaction catalyzed by a Cr^{III} complex

Leila Yu. Ustynyuk*[a] and Alexander F. Shestakov[b]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. E-mail: leila_ust@mail.ru*
[b] *Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation*

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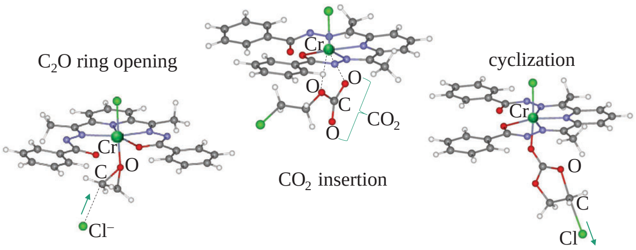
The mechanism of the carbon dioxide and alkene oxide reaction catalyzed by the pentagonal-bipyramidal Cr^{III} complex, dichloro[2,6-diacetylpyridine bis(benzoylhydrazone)(1−)]chromium, includes the steps of sequential binding of the epoxide molecule, chloride ion and CO_2 with the catalytic particle and subsequent cyclization, accompanied by dissociation of Cl^-. The solvent effect is important for the formation of the cyclic carbonate product.

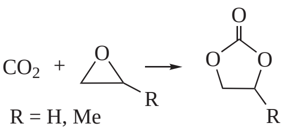


Keywords: Cr^{III} complexes, carbon dioxide, epoxides, DFT, modeling.

Pentagonal-bipyramidal Cr^{III} complexes are known as catalysts for the reactions of CO_2 with epoxides.[1–3] A distinctive feature of these complexes is that they provide a high yield of cyclic carbonates and a low yield of polycarbonates, unlike other complexes, in particular (salen)Cr^{III}.[4,5] The reaction proceeds at temperatures of 60–80 °C in liquid propylene oxide in the presence of an ionic cocatalyst, bis(triphenylphosphine)iminium chloride, the optimal catalyst–cocatalyst ratio is 1 : 2.

In this work, a density functional theory (DFT) approach was used to model the formation of a cyclic carbonate from CO_2 and epoxide (Scheme 1). Ethylene oxide was used as the simplest model of the epoxide molecule. Since charged species such as Cl^- are involved in the reaction, the solvent effect was taken into account in this study to calculate the energy profile of the reaction. For all the structures considered here, a solvent model consisting of 6–12 discrete ethylene oxide molecules was used, and a similar model of propylene oxide was used to calculate the solvation energy of Cl^-.

The DFT method is widely used to model reactions catalyzed by transition metal complexes. We used the non-commercial program ‘Priroda’, developed for fast quantum chemical calculations,[6,7] and the PBE96 functional,[8] which is known to be useful for studying transition metal complexes. The orbital basis sets for solving the Kohn–Sham equations are contracted Gaussians with the following contraction patterns: $(17s\,13p\,8d)/[12s\,9p\,4d]$ for Cr, $(15s\,11p\,2d)/[10s\,6p\,2d]$ for Cl, $(11s\,6p\,2d)/[6s\,3p\,2d]$ for N, C and O, as well as $(5s\,1p)/[3s\,1p]$ for H. All structures presented here are fully optimized. The type of stationary point on the potential energy surface (PES) of the system was determined from the vibrational spectra of the structure.



Scheme 1

The Cr^{III} complex, dichloro[2,6-diacetylpyridine bis(benzoylhydrazone)(1−)]chromium† **1** (Scheme 2), can form a number of isomers and conformers. Among them, structure **1** is the most stable, according to calculations in the gas-phase approximation, due to the formation of an intramolecular hydrogen bond O–H···Cl. In the crystal, the structure of the complex differs from structure **1**: the pentadentate equatorial ligand is plane, and the hydrogen atom H moves to the nitrogen atom N.[1] There is a local minimum corresponding to such an isomer of complex **1** on the PES of the system, but its energy is higher by 5.3 kcal mol^{-1}. In the crystal, this form is stabilized by intermolecular hydrogen bonds N–H···Cl.

In accordance with the experimental data,[2] quantum chemical calculations led to the conclusion that the most stable state of the Cr^{III} complex **1** corresponds to the total spin $S = 3/2$. The spin state of the system does not change in the course of the catalytic reaction studied here.

As is known from published data, for example, for (salen)Cr^{III} complexes,[4,5] the catalytic particle must have a coordination vacancy in the axial position with respect to the Cr atom. According to our data, the catalytic particle of structure **2** can be formed from dichloride complex **1** by reaction (1) (see Scheme 2). Reaction (1) is exothermic with a negative energy effect $\Delta E(1) = -4.5$ kcal mol^{-1}. The detailed mechanism and energy profile of reaction (1) will be published elsewhere.

The reaction mechanism includes several steps. The first step is the coordination of the epoxide molecule by catalytic particle **2**, resulting in the formation of adduct **3**. The second step is the

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† IUPAC name: dichloro[({1-[6-(1-{[hydroxy(phenyl)methylidene]hydrazinylidene}ethyl)pyridin-2-yl]ethylidene}hydrazinylidene)phenylmethanolato]chromium^{III}.

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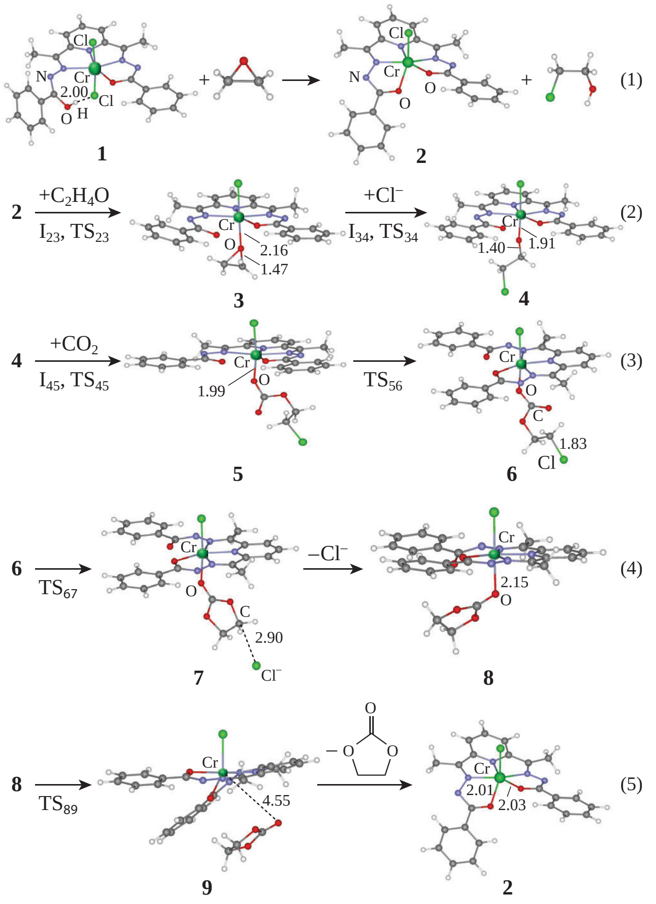

Scheme 2

opening of the C_2O cycle induced by the addition of a chloride ion, leading to the formation of a negatively charged compound **4** [Scheme 2, reaction (2)]. The next step is the insertion of a CO_2 molecule into the Cr–O bond of the Cr–OCH_2CH_2Cl fragment and the formation of compound **5**. Internal rotation around the CrO–C(O)O bond of the Cr–$OC(O)OCH_2CH_2Cl$ fragment reduces the energy of the system by 1.8 kcal mol^{-1}, leading to more stable conformer **6** [Scheme 2, reaction (3)]. The energy barrier of internal rotation is 1.5 kcal mol^{-1} relative to the less stable conformer **5**. The next step is the formation of new C–O bond in conformer **6**. The terminal O atom of the C=O group participates in the cyclization. A weak electrostatic complex **7** is formed, which dissociates into Cl^- and uncharged product **8** [Scheme 2, reaction (4)]. At the final step [reaction (5)], the cyclic carbonate dissociates from the Cr^{III} complex and catalytic particle **2** is released. The terms TS_{lm} and I_{lm} in Scheme 2 denote a transition state and an intermediate in the reaction path between the structures with numbers **l** and **m**, respectively. Selected interatomic distances are shown in angstroms. Optimized structures of key transition states along the reaction path are shown in Figure S1 (see Online Supplementary Materials).

The calculated energy effect of the formation of cyclic carbonate from CO_2 and C_2H_4O (see Scheme 1) is $\Delta E = -16.7$ kcal mol^{-1}. The ZPE corrections change this value to $\Delta E_0 = -13.1$ kcal mol^{-1}. The energy profile (Figure 1, profile *1*) is calculated for the mechanism presented in Scheme 2 in the gas-phase approximation. The asterisks show the energies of the structures with ZPE corrections. The systematic deviation of the energy profiles without and with the ZPE corrections is due to the difference in the energy effects of the reaction ΔE and ΔE_0.

At the steps of binding [reaction (2)] and dissociation [reaction (4)] of the negatively charged chloride ion, the total energy of the system drops and rises by 28.4 ± 2.1 kcal mol^{-1}, respectively. This result contradicts the experimentally observed formation of a cyclic product: the reaction in the gas phase would stop after the formation of the most stable compound **6**. Only products of subsequent insertions could be formed. To improve the agreement between the results of calculation and experiment, it is necessary to take into account solvent effects.

Two types of solvent effects were considered here. The most important correction of the energy profile *1* (see Figure 1) is to take into account the energy of Cl^- solvation at stages (2)–(4) (see Scheme 2). To do this, the chloride ion was surrounded by *n* ethylene oxide molecules, which were added to the system by two molecules, followed by total optimization of the system geometry at each step of addition. For each structure, Cl^- was removed from the solvent shell and the structure of the cluster consisting of *n* epoxide molecules was optimized.

For each system with *n* epoxide molecules, $\Delta E_{solv}(Cl^-)$ was estimated as the difference between the sum of the energies of an isolated chloride ion and a cluster of *n* epoxide molecules and the energy of a Cl^- ion surrounded by *n* epoxide molecules, according to the equation:

$$\Delta E_{solv}(Cl^-) = E(Cl^-) + E(nC_2H_4O) - E(Cl^- \cdot nC_2H_4O).$$

The relationship between the value of $\Delta E_{solv}(Cl^-)$ and the number of solvent molecules *n* reaches a steady state level at $n > 10$ (Figure S2). Ten is the maximum number of epoxide molecules in the first coordination sphere of Cl^-, further molecules added to the system fill the second coordination sphere and have little effect on the value of $\Delta E_{solv}(Cl^-)$. For $n = 12$, $\Delta E_{solv}(Cl^-) = 40.6$ kcal mol^{-1}. This value was added to the energy of each of the structures between the steps of Cl^- binding to the Cr complex and its dissociation. The $\Delta E_{solv}(Cl^-)$ corrected energy profile *2* is shown in Figure 1.

Since propylene oxide was used in the experimental study,[1] $\Delta E_{solv}(Cl^-)$ values were calculated for 4 and 8 propylene oxide molecules. These values are close to the corresponding values for ethylene oxide. For example, at $n = 8$, the values of $\Delta E_{solv}(Cl^-)$ are 37.3 and 36.6 kcal mol^{-1} for ethylene and propylene oxides, respectively.

Energy profile *2* (see Figure 1) explains the formation of the cyclic carbonate product and highlights the three highest transition states along the reaction path. The first is the transition state TS_{34} at the C_2O cycle opening step, the second transition state TS_{45} occurs at the CO_2 molecule insertion step, and the third is the transition state TS_{67} at the cyclization step. However, the values of these energy barriers are still incorrect. Their structures were optimized in the gas-phase approximation. Whereas in solution, the solvent could change the energies of transition states and other structures along the reaction path, depending on the total electron charge of the structure and the electron charges on the atoms.

A second type of solvent correction ΔE_{solv} was calculated for each structure (stable compound, intermediate or transition state) on the reaction path using the above formula. Six molecules of ethylene oxide were used to surround the fragments and particles involved in the reorganization of atomic bonds. Since these fragments and particles are always located on one side of the equatorial ligand, all molecules were located on the same side of the complex.

Figure 1 (inset) demonstrates the optimized structure of transition state TS_{34} of the C_2O cycle opening step. The chloride ion surrounded by six C_2H_4O molecules binds to the seventh C_2H_4O molecule coordinated to the Cr ion. The solvation energy $\Delta E_{solv}(TS_{34}) = 17.2$ kcal mol^{-1} is the highest value among other structures on the reaction path. The geometry parameters of structure TS_{34} differ from the parameters of the same transition state optimized in the gas-phase approximation (no C_2H_4O molecules were added). Thus, the C–Cl and C–O distances in the 'solvated' TS_{34} (see Figure 1, inset) are 2.54 and 1.76 Å, respectively,

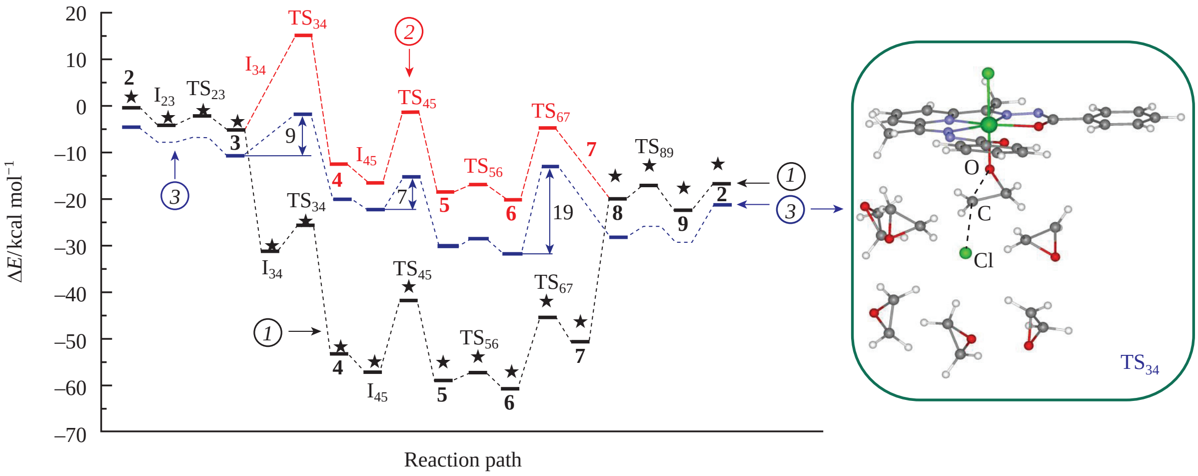

Figure 1 Energy profiles of the reaction of ethylene oxide with CO_2 catalyzed by the Cr^{III} complex **2** (see Scheme 2): (*1*) profile calculated in the gas-phase approximation with (★) and without (‑) ZPE corrections; (*2*) profile *1*, corrected for the solvation energy of the chloride ion; (*3*) profile *2*, corrected for the solvation energies of all structures along the reaction path. The inset shows an optimized structure of transition state TS_{34} for epoxide ring opening with six epoxide molecules surrounding an attacking chloride ion.

while in the ‘isolated’ TS_{34} structure these distances, 2.98 and 1.53 Å, are markedly different. Therefore, the ‘solvated’ transition state lies closer to product **4** along the reaction coordinate.

For the transition state at the step of CO_2 insertion into the Cr–O bond, we obtained $\Delta E_{solv}(TS_{45}) = 14.1$ kcal mol^{-1}, and for the cyclization step, $\Delta E_{solv}(TS_{67}) = 8.4$ kcal mol^{-1}. The ΔE_{solv} values are more significant for negatively charged structures than for uncharged ones. The solvation energies ΔE_{solv} calculated for structures with six C_2H_4O molecules were subtracted from the energies of profile *2* for the same structures. Energy profile *3* was constructed (see Figure 1), which takes into account two types of solvent corrections.

Transition state TS_{34} maintains a global maximum at energy profile *3*. The relative energies of transition states TS_{34}, TS_{45} and TS_{67} differ from those for energy profile *2*. The differences between the energies of transition states TS_{34}, TS_{45} and TS_{67} and their preceding stable structures corresponding to local PES minima are 9, 7 and 19 kcal mol^{-1}, respectively. With the ZPE corrections, we obtained 7, 8 and 18 kcal mol^{-1} for TS_{34}, TS_{45} and TS_{67}, respectively. The first and second transition states correspond to bimolecular, and the third – to monomolecular transformations. There are no sufficiently high energy barriers on the reaction path that prevent the reaction from proceeding under experimental conditions (liquid propylene oxide as a solvent, temperature range 60–80 °C). Thus, the reaction mechanism discussed above is in good agreement with the experimental data.[1]

Although the pentagonal-bipyramidal Cr^{III} complex studied here by DFT method has its own structural features compared to other previously studied Cr complexes, the results of this study are in good agreement with the basic concept of the mechanism of CO_2 fixation by epoxides catalyzed by transition metal complexes. The role of the cocatalyst as a donor of Cl^- ions at the step of C_2O cycle opening has been widely discussed in the literature.[4,5,9–11] Future modeling of the copolymerization of CO_2 with epoxides might shed light on the reason for the predominance of the cyclic product among the two possible products of the catalytic reaction.[1] This could be due to steric hindrance for the insertion of the second epoxide molecule arising from the pentadentate structure of the equatorial ligand compared to the tetradentate structure of the (salen)Cr^{III} complexes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.09.006.

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